Reactivity of lignin model compounds through hydrogen transfer catalysis in ethanol/water mixtures

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ABSTRACT

The conversion of lignin into useful bio-based chemicals and fuels requires a fundamental understanding of the reaction mechanisms involved in the cleavage of the specific chemical bonds that constitute its polymeric structure. The catalytic conversion of eight lignin model compounds emulating various C—O and C—C bond of lignin was explored in a batch reactor with a Pt/C catalyst in ethanol/water mixtures, using ethanol as both H-donor and solvent. The order of reactivity for hydrogenolysis of C—O model bonds was found: β—O—4 > α—O—4 » 4—O—5, the 4—O—5 bond exhibiting a very low reactivity. Phenolic hydroxyl and methoxyl groups were unreactive, whereas aliphatic hydroxyl groups could be eliminated by dehydration, leading to an overall partial deoxygenation. α-1 model C—C bonds were also cleaved by hydrogenolysis, but β-1 model C—C bonds were not. The cleavage of C—O and C—C bonds obtained by H-transfer catalysis in water-ethanol mixtures was very selective, intermediate products were sometimes detected before full reaction completion but no decomposition or degradation products.

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1. Introduction

Lignin is produced in large amounts as by-product of the Kraft and paper industry, but only a small part of it is used as dispersants, emulsifiers, for partial replacement of phenol in phenol-formaldehyde resins, production of vanillin, while the largest current use of industrial lignins is as low heating value fuel for energy supply [1]. Lignin is a natural polymer based essentially on three monolignol monomers, coniferyl, coumaryl and sinapyl alcohols, randomly cross-linked through various types of ether and C—C bonds. With its high aromatics content, lignin could provide a renewable source of monomeric aromatic compounds and fuels, but its composition is complex and differs from one sample to another, preventing an in-depth understanding of its reactivity. Lignin transformation into useful products requires efficient processes to cleave selectively the various chemical bonds that contribute to its high stability and resistance to chemical degradation.

Since biomass always contains water, biomass conversion technologies, such as fast pyrolysis or hydroliquefaction, yield a mixture of organic compounds and water. Separation of water, purification and drying represent costly steps in biomass-based industrial processes. Therefore, aqueous phase catalytic conversion of bio-based products can provide a cost-effective strategy to the development of biomass-based chemicals and fuels [2,3]. Water is also an ideal solvent according to the "green chemistry" principles.

The reductive bond cleavage approach to lignin (or model compounds) bond cleavage using homogeneous catalysts with hydrogen or silanes as reducing agents is well documented [4]. Although cleavage can be effective under rather mild temperature and pressure conditions (80–150 °C, atmospheric pressure or slightly higher), large amounts of strong bases such as alkali metals alcoholates are also required [3]. Heterogeneous catalytic systems have also been widely investigated for lignin or lignin model compounds hydroprocessing under hydrogen [5,6], allowing more severe reaction conditions than homogeneous catalysts (typically, 250–450 °C and 10–200 bar). Depending on the reaction conditions, hydrogenolysis and/or hydrodeoxygenation products are obtained.

Hydrogen transfer from organic H-donors such as alcohols or formic acid is an attractive alternative to using high-pressure hydrogen, which presents important safety and handling issues [7]. Levulinic acid can be selectively reduced to γ-valerolactone using isopropanol as H-donor and Ni-based bifunctional catalysts [8]. In addition, alcohols, and particularly ethanol, can be produced from renewable sources. In a previous study, we reported the catalytic conversion of eugenol, chosen as lignin model compound,

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in high-pressure ethanol/water mixtures [9]. The aim of the current investigation is to gain insight into the reactivity of eight other model compounds, chosen to emulate prevalent C—O and C—C linkages present in lignin. Some of these model compounds have been studied before, often under different reaction conditions. The objective here is to understand the catalyst role, the reactions involved and the effect of substituents or insaturations on the considered linkage. Apparent activation energies were determined from catalytic runs at different temperatures, allowing a comparison of the model compounds reactivity.

2. Experimental

2.1. Catalyst preparation

The carbon support (Engelhard) was previously calcined at 500 °C under N_2 for 5 h. $Pt(NH_3)_4(OH)$ was supplied by Alfa Aesar. The Pt salt was deposited on the supports by wet impregnation in water during 30 min in order to obtain a loading of 2 wt.% Pt on the support. Water was evaporated in a rotatory evaporator and the catalyst was calcined at 500 °C in air to decompose the metal salt. Platinum were then reduced under hydrogen at 300 °C for 2 h.

2.2. Catalyst characterization

The Pt loading on the carbon support was analysed by ICP-OES. The 2 wt.% Pt/C catalyst used in kinetic studies had a specific surface area of 970 m^2 g^{-1}, with a mean particle size of 16 μm (measured by Laser diffraction particle size analysis). The catalyst porosity was characterized by nitrogen physisorption using a 3Flex Micrometrics analyzer. The catalyst was essentially microporous (≈80% of BET surface area, pore size around 0.6 nm) with a small amount of mesopores with a pore size around 2.3 nm, actually very close to micropores. Pt leaching was assessed by hydrothermal ageing of Pt/C catalyst in water at 320 °C for 3 h. The Pt content in water after ageing analysed by ICP-OES was 0.1 ppm, which represented less than 0.006% of the total Pt amount. TEM images of fresh and post-run catalyst used under similar conditions can be found in [21].

2.3. Reactor and kinetic studies

All chemicals and model compounds were obtained from commercial suppliers and used as received. The reactions were performed in a 250 mL Hastelloy autoclave (Parr) equipped with high-pressure valves for liquid or gas introduction and sampling, a pressure indicator and a magnetically coupled stirrer drive. Runs were performed under autogenous pressure, which depended on the applied temperature. In a typical experiment, the reactor was loaded with water and the desired amount of catalyst, then purged by bubbling nitrogen in the water for 10 min in order to remove gaseous air and dissolved oxygen. The reactor was heated to the intended temperature; after temperature stabilization, the solution of model compound in ethanol was injected in the autoclave using a preparative HPLC pump (maximum flow rate 100 mL/min, maximum pressure 275 bar). The injection time was 2 min. The total liquid volume loaded in the autoclave was always 150 mL. The stirring rate was set to 300 rpm. In tests performed at 600 rpm the reaction rate was not modified, showing therefore that the reaction was not limited by external mass transfer at 300 rpm. Liquid samples (1 mL) were periodically collected through a liquid sampling valve and were analysed by GC–MS.

2.4. GC/MS analysis

The model compounds and their reaction products were analysed by GC/MS (Shimadzu QP 2010) on a Zebron ZB-WAX-Plus column (60 m × 0.25 mm × 0.25 μm). The injected volume was 0.5 μL, to prevent exceeding the liner volume during vaporization of water. The GC oven temperature was programmed from 45 °C to 250 °C (15 min) with a heating rate of 10 K/min. The split ratio was 300:1, except for the analyses of guaiacylglycerol-β-guaiacylether, which were performed in splitless mode due to the low concentrations. The interface temperature between the chromatograph and the mass spectrometer was 260 °C and the ion source was maintained at 250 °C. The mass detector was briefly shut off during analysis, when the solvent peak eluted from the column, to prevent signal saturation.

3. Results and discussion

3.1. Lignin model compounds

The model compounds studied are shown in Fig. 1. These compounds are solids at room temperature. They were chosen to represent the typical linkage groups of lignin, but also their solubility in ethanol and the ability to analyse them by GC–MS.

1-(2,4-dihydroxyphenyl)-2-(4-methoxyphenoxy)-ethanone (DHPMPE) and guaiacylglycerol-β-guaiacylether (GGGE) were chosen as models for the β-O-4 linkage of lignin, which is the most frequent linkage in lignin (50–60%). The calculated bond dissociation enthalpy (BDE) for the homolytic cleavage of this bond was found equal to 250–290 kJ/mol [10,11], but the oxidation of OH substituents on the aliphatic chain into ketones decreased significantly the BDEs to an average value of ≈235 kJ/mol [10].

The α—O—4 linkage accounts for 4–8% of the total linkages of lignin, whereas the Cα—O bond is considered as the most easily cleaved, with an average BDE around 235 kJ/mol [9,10]. Benzylphenylether (BPE) was used to represent this linkage.

The 4—O—5 linkage of lignin is present from 4 to 8% in both softwood and hardwood [4]. It was emulated with 4-phenoxyphenol (4PP). This C_{aryl}—O—C_{aryl} ether bond is more stable than the previous and exhibits a bond dissociation enthalpy of 334 kJ/mol [12].

The C—C linkages represent 25–33% of the bonds present in lignin [13], and they are more difficult to cleave than C—O bonds [10]. They are more abundant in processed lignins such as Kraft lignin: in the harsh conditions of the Kraft pulping process, lignin is depolymerized by radical reactions that break C—O ether bonds, but radical coupling reactions also form highly stable C—C bonds that were not present in the native lignin [14]. The computed BDEs for the β-5 linkages were found around 430 and 440 kJ/mol for C—Cα and C—Cβ cleavage, respectively. For biphenyl-type bonds, the BDE was close to 480 kJ/mol [10]. Bibenzyle (BBZ) was selected to mimic a β-1 linkage, whereas with α-phenylcinnamic acid (PCA) the Cα=Cβ bond is unsaturated and Cβ is substituted with a carboxylic group.

Bisphenol A (BPA) and bisphenol F (BPF) were chosen to emulate α-1 linkages, with two methyl groups on the Cα carbon for BPF. Contrary to earlier reports, no α-1 linkages could be detected in native lignin using modern analytical NMR techniques such as HSQC. However, they are formed by recombination of the degradation intermediates/monomers after cleavage of β—O—4 linkages, leading to the repolymerization of lignin with an increased molecular weight and heterogeneity [5,15].
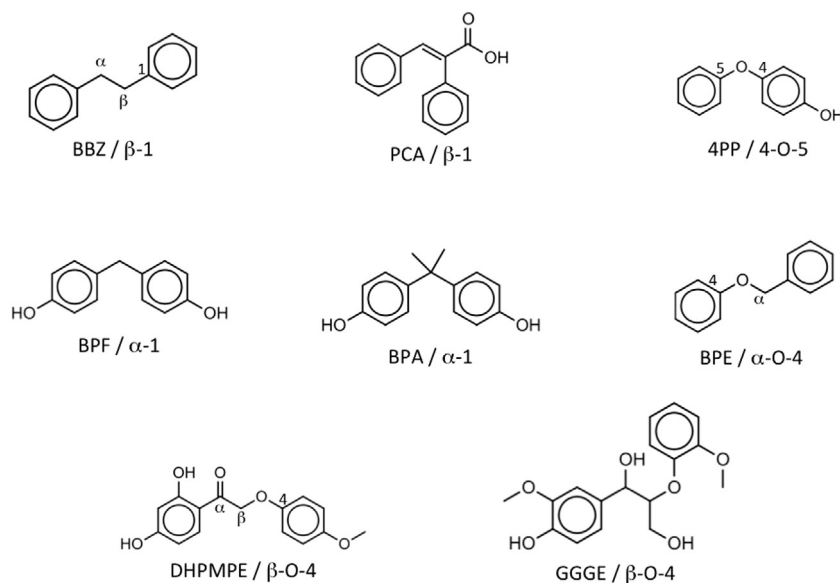
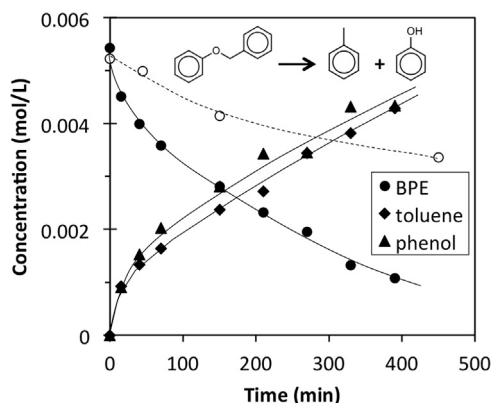**Fig. 1.** Model compounds selected for catalytic hydrothermal conversion studies.

Fig. 2. Comparison of BPE reaction profiles in ethanol-water mixture with and without catalyst. Black symbols: with 3.70 mg Pt/C catalyst; empty circles: BPE disappearance, no catalyst. Conditions: 1 g/L BPE in 50 vol.% ethanol + 50 vol.% water, 300 °C, P = 120 bar.

Fig. 3. Effect of initial BPE concentration on the rates of BPE disappearance and product formation. Conditions: 0.25, 0.5 or 1 g/L BPE in 50 vol.% ethanol + 50 vol.% water, 3.72 ± 0.04 mg Pt/C, 300 °C, 120 bar.

3.2. Hydrothermal conversion of model compounds with C—O linkages

The reaction profile of benzylphenylether (BPE) in water/ethanol in the presence of Pt/C catalyst at 300 °C is shown in Fig. 2. The reaction produced only toluene and phenol in equimolar amounts, suggesting that H-transfer hydrogenolysis of the Cα—O bond was the sole reaction pathway. Indeed, a hydrolysis route would lead to the formation phenol and benzyl alcohol. For comparison, the rate of BPE disappearance in the absence of catalyst under similar conditions is shown as the empty symbols connected by a dotted line (similar products were formed, not shown). The catalyst clearly enhanced the reaction rate, but did not modify the products selectivity.

In this reaction, ethanol was the hydrogen donor through its dehydrogenation into acetaldehyde. Acetaldehyde formation was identified in specific analyses where the samples were analysed immediately after withdrawal from the autoclave, while the GC oven temperature programme was started at 45 °C. An accurate quantification of acetaldehyde, however, could not be achieved because it is hig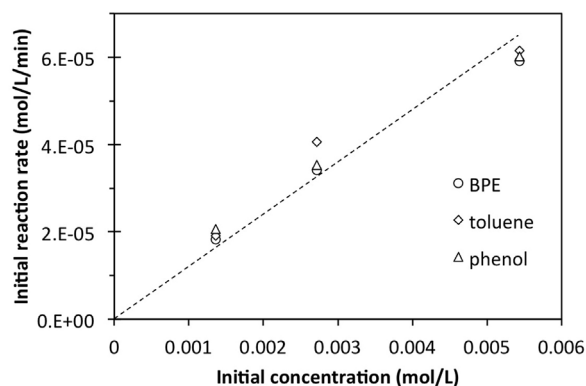hly volatile (boiling point 20.8 °C) and evaporates during sampling (which is performed at the reaction temperature), leading to irreproducible analyses.

Kim et al. studied the cleavage of BPE in hexadecane at 250 °C under 10 bar H₂, using a Pd-Fe catalyst supported on an ordered mesoporous carbon [16]. Toluene and phenol were the main products, but ethylbenzene, methylcyclohexane and ethylcyclohexane were also formed in significant amounts. In contrast, in our experiments, H-transfer from ethanol was more selective, since only the Cα-O bond was cleaved, but also milder since no products resulting from the hydrogenation of the aromatic ring were formed.

Catalytic tests starting with different initial concentrations of BPE revealed that the rates of BPE consumption and products formation varied linearly with the initial BPE concentration, in agreement with first order kinetics (Fig. 3).

The effect of reaction temperature on the rate of BPE disappearance is depicted in Fig. 4. At 325 °C, BPE was fully converted in less than 100 min. At all temperatures, the reaction products were only phenol and toluene (data not shown). The calculated apparent energy for BPE hydrogenolysis was 99 kJ/mol, evidencing the catalyst impact on the reaction mechanism (235 kJ/mol for homolytic cleavage of α—O—4 bonds).
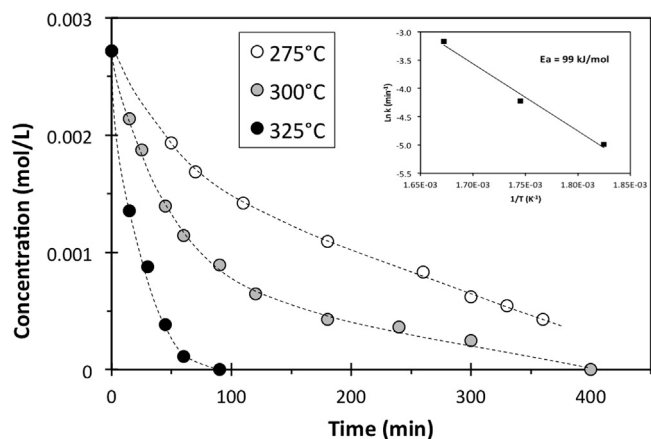
Fig. 4. Reaction profiles of BPE at three temperatures. Insert: Arrhenius plot of rate constants vs. temperature and calculated apparent activation energy. Conditions: 0.5 g/L BPE in 50 vol.% ethanol + 50 vol.% water, 3.70 ± 0.04 mg Pt/C, 80 bar at 275 °C, 120 bar at 300 °C, 180 bar at 325 °C.
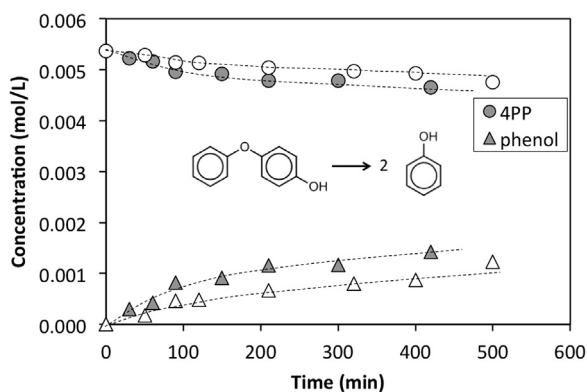

Fig. 5. Reaction profile of 4PP in ethanol-water mixture. Grey symbols: with 3.74 mg Pt/C catalyst; white symbols: no catalyst. Conditions: 1 g/L 4PP in 50 vol.% ethanol + 50 vol.% water, 325 °C, 180 bar.

The conversion of 4-phenoxyphenol (4PP) at 325 °C under similar conditions is depicted in Fig. 5. For comparison, the reaction profile obtained in the absence of catalyst is included. Phenol was the only product formed, as the result of C_4—O bond H-transfer hydrogenolysis. The effect of Pt/C catalyst was limited, the conversion of 4PP increasing only slightly in the catalyst presence. 4PP appeared much less reactive than BPE, since its conversion reached only ≈13% after 420 min at 325 °C, whereas BPE was fully converted in less than 100 min at the same temperature (Fig. 4). The ether C_{aryl}—O bond was clearly very stable. Indeed, the bond dissociation energy of diphenylether is almost 100 kJ/mol higher than that of benzylphenylether (314 and 218 kJ/mol, respectively) [17]. Interestingly, there was no cleavage of the second C—O bond that would lead to the formation of benzene and 1,4-dihydroxybenzene, which suggests that the electronegative hydroxyl substituent weakened the C_4—O bond.

He et al. [16] studied the mechanism of aqueous C—O bond cleavage in diphenylether, di-p-tolylether and 4,4′-dihydroxydiphenylether over Ni/SiO_2 at 120 °C under 6 bar H_2, using kinetic data and DFT calculations. Hydrogenolysis and hydrolysis of the ether bond were proposed as the main reaction pathways, but subsequent hydrogenation of the aromatic rings also took place. These hydrogenation products were not observed here, in spite of the more severe temperature and pressure conditions, but no molecular hydrogen was available.

An apparent activation energy of 130 kJ/mol for the conversion of 4PP was calculated from runs at different temperatures (Fig. 6).
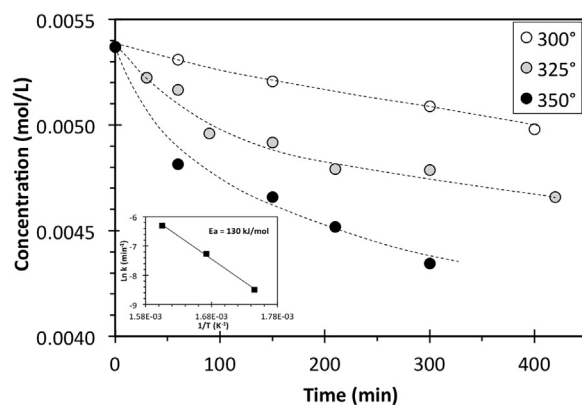

Fig. 6. Reaction profiles of 4PP at three temperatures. Insert: Arrhenius plot of rate constants vs. temperature and calculated apparent activation energy. Conditions: 1 g/L 4PP in 50 vol.% ethanol + 50 vol.% water, 3.70 ± 0.04 mg Pt/C, 120 bar at 300 °C, 180 bar at 325 °C, 240 bar at 350 °C.
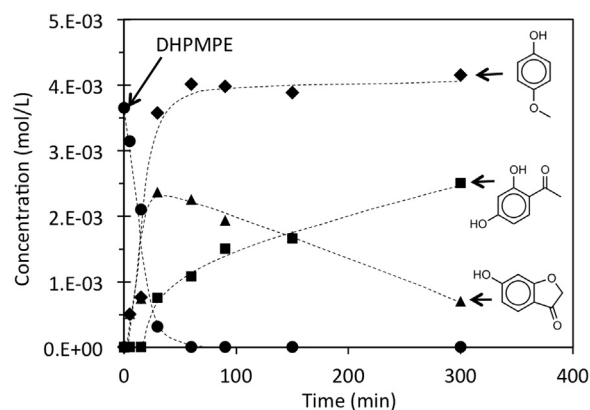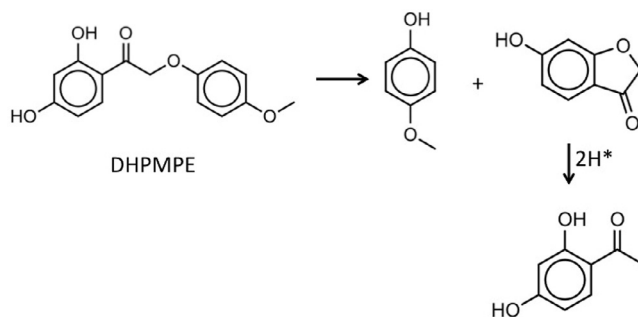

Fig. 7. Reaction profile of DHPMPE in ethanol-water mixture. Conditions: 1 g/L DHPMPE in 50 vol.% ethanol + 50 vol.% water, 18.69 mg Pt/C, 275 °C, 80 bar.

Scheme 1. Reaction network for DHPMPE in water-ethanol mixture.

The cleavage of the β-O-4 linkage was investigated using DHPMPE (Fig. 1) as model compound. The reaction profile of DHPMPE at 275 °C (Fig. 7) revealed the rapid cleavage of the β-O-4 linkage, yielding quantitative amounts of 4-methoxyphenol and a mixture of 6-hydroxy-3-coumaranone and 2,4-dihydroxyacetophenone. At the reaction onset (<15 min), only the coumaranone and 4-methoxyphenol were formed with similar rates, suggesting that the first step consisted in a simple cleavage of the β-O-4 bond with simultaneous cyclisation of the dihydroxyacetophenone fragment into 6-hydroxy-3-coumaranone (Scheme 1) favoured by the presence of the OH group in α position on the aromatic ring. H-transfer hydrogenolysis of the pentacyclic ether bond subsequently yielded 2,4-dihydroxyacetophenone.
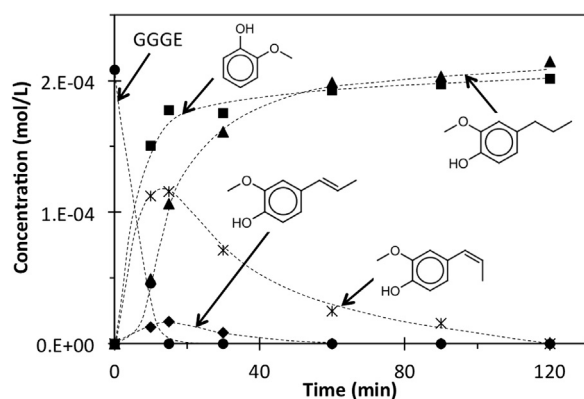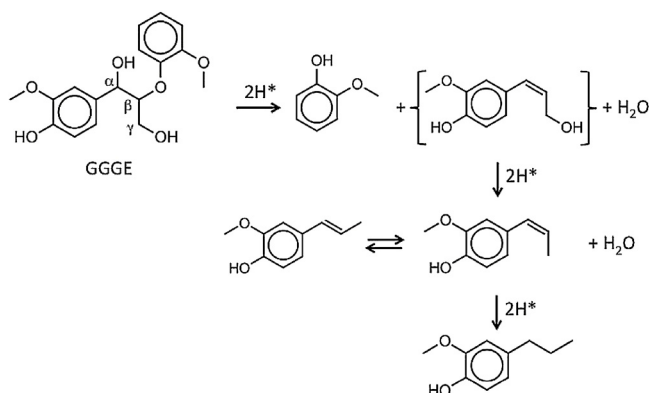
Fig. 8. Reaction profile of GGGE in ethanol-water mixture. Conditions: 0.067 g/L GGGE in 50 vol.% ethanol + 50 vol.% water, 5.12 mg Pt/C, 275 °C, 80 bar.

Scheme 2. Reaction network for GGGE in water-ethanol mixture.

Similar runs performed at 250 and 300 °C (data not shown) provided the apparent activation energy for the conversion of DHPMPE, 58 kJ/mol. This was significantly lower than the apparent activation energy for BPE and 4PP C—O bond H-transfer hydrogenolysis (99 and 130 kJ/mol, respectively); increasing the alkyl chain length between the aromatic rings clearly enhanced the reactivity of the ether bond, since it allowed H abstraction on the Cα or Cβ carbons to form reactive intermediate species.

To assess the effect of substituents on the Cα and Cβ carbons of the β—O—4 linkage, the reaction of guaiacylglycerol-β-guaiacylether (GGGE) with Pt/C catalyst in water/ethanol was also investigated. In this compound, the Cα carbon is sp^3 and bears a hydroxyl group, whereas the Cβ carbon is linked to an hydroxymethyl group (cf. Fig. 1).

As seen in Fig. 8, the Cβ—O bond was rapidly cleaved to yield 2-methoxyphenol (guaiacol) and 4-propyl-2-methoxyphenol as the main products. Intermediately, the two Z and E isomers of 4-propenyl-2-methoxyphenol were also detected, but they were clearly intermediate compounds leading to 4-propyl-2-methoxyphenol as final product. This means that the two hydroxyls remaining on Cα and Cγ, after scission of the guaiacol fragment from Cβ, were very rapidly eliminated by dehydration to give 4-propenyl-2-methoxyphenol (Scheme 2).

Dehydration reactions are very often encountered with sugars, even when the reaction medium is water [2]: the dehydration of glucose, fructose or xylose is an important reaction to convert C_6 and C_5 sugars into the platform molecules furfural and HMF. The dehydration of the secondary OH on Cα should be favoured over the primary OH on Cγ because the dehydration of secondary alcohols is easier than primary alcohols. Nevertheless, those two steps were very rapid, since the intermediate com-

pound 4-(3-hydroxypropenyl)-2-methoxyphenol (resulting from OH on Cα elimination) was not detected. The second dehydration step favoured the formation of 4-(1-propenyl)-2-methoxyphenol rather than the terminal olefin 4-(2-propenyl)-2-methoxyphenol, in agreement with Zaïtzev rule. The two Z and E isomers of 4-(1-propenyl)-2-methoxyphenol were in equilibrium, the E form being detected only in small amounts with a constant E/Z ratio (≈12%). In a previous study on the reaction of eugenol under similar conditions [8], we already evidenced the rapid interconversion of these two isomers with the same equilibrium ratio.

Runs performed at 250 and 300 °C (data not shown) allowed calculating the apparent activation energy for the reaction of GGGE: 55 kJ/mol. This was close to the apparent activation energy for the reaction of DHPMPE (58 kJ/mol), suggesting that the substituents on Cα and Cβ carbons of the β—O—4 bond played only a minor role in the reactivity of this linkage. As a matter of comparison, Parker et al. [18] reported apparent activation energies of 66 and 96 kJ/mol for the cleavage of GGGE in DMSO using two different V-based homogeneous catalysts.

The relatively low apparent activation energy found for the H-transfer hydrogenolysis of the β-O-4 bonds of both DHPMPE and GGGE can be related to the results obtained by Ma et al. on the catalytic ethanolysis of Kraft lignin in supercritical ethanol [19]: high yields in monomeric phenolic compounds were obtained, suggesting that the cleavage of the β-O-4 bond is probably an important reaction pathway for the reductive lignin depolymerisation, not only because the β-O-4 bonds are the most abundant in lignin, but also because they are the weakest towards hydrogenolysis.

Within the four model compounds of lignin with C—O linkages studied here, GGGE was actually the only one leading to an overall reduction of the oxygen content through the dehydration of one of its fragments (2 oxygen atoms removed in a total of 6). In comparison, the oxygen of the Cα = carbonyl group in DHPMPE was not removed under similar conditions, probably because the conjugation with the aromatic ring enhanced its stability. Whatever the molecule studied, Ph-OH or Ph-OMe bonds were not cleaved under the present conditions, confirming our earlier results on eugenol [8]. These results are consistent with the high bond dissociation energies calculated for these bonds: 450 and 383 kJ/mol, respectively [20]. The C_{aryl}—O—C_{aryl} ether bond in 4PP was hardly cleaved at 325 °C. We have shown previously, however, that linoleic acid can be deoxygenated under similar conditions through H-transfer hydrogenolysis of its ester [21]. A more general picture emerges now regarding the possible deoxygenation pathways for biomass model compounds under hydrogen transfer conditions: the easiest deoxygenation pathways are the dehydration of aliphatic OH and the loss of carboxylic groups. Oxygen atoms linked to aromatic rings or conjugated with an aromatic ring do not react. Similarly, Klein et al. [22] showed that under mild HDO conditions (225 °C, in pure methanol + 34 bar H_2, with Pd/C as catalyst and Zn(OAc)$_2$ as co-catalyst) and despite the use of high pressure hydrogen, GGGE was cleaved but the removal of oxygen was limited to the elimination of OH groups at Cα and Cγ positions.

This study also revealed that the reactions performed in water/ethanol mixtures were highly selective towards hydrogenolysis/hydrogenation products, without any formation of by-products originating from decomposition or condensation reactions. Similarly, Ma et al. [18] found that the ethanolysis of Kraft lignin in supercritical ethanol yielded selectively monomeric compounds, rather than dimeric or oligomeric compounds, and that no tar or char were formed. Compared with lignin hydrothermal conversion in pure water, which favours homolytic bond cleavage leading to radical formation, using alcohols as solvents is known to increase reaction rates and to prevent re-polymerization reactions [5,23], since they favour heterolytic bond cleavage. Of direct relevance to the present study, Guo et al. reported the cleavage of the
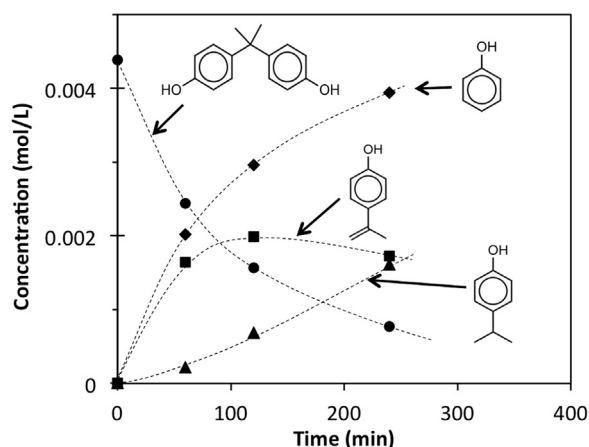
Fig. 9. Reaction profile of BPA in ethanol-water mixture in the absence of catalyst. Conditions: 1 g/L BPA in 50 vol.% ethanol + 50 vol.% water, 300 °C, 120 bar.

Cβ-O bonds of 2-(2-methoxyphenoxy)-1-phenylethanol, a β-O-4 lignin model compound, over a WC/carbon catalyst under ≈7 bar H₂ in various organic solvents and water [24]. When run in pure THF, toluene, dioxane or water, severe side reactions occurred, leading to high amounts of side products and unidentified compounds. Although much more selective when run in methanol or ethanol, the reaction still produced noticeable amounts of by-products. Interestingly, the most selective reaction conditions were those where hydrogen had been replaced by argon and the solvent was methanol. Our results demonstrate that hydrogen-transfer from ethanol using an appropriate catalyst provides a very efficient and selective route to the cleavage of C—O bond of lignin.

3.3. Hydrothermal conversion of model compounds with C—C linkages

Bisphenol A (BPA) was chosen to emulate an α1 linkage of lignin. This compound is symmetrical, each aromatic ring bearing one hydroxyl group in the para position. The reaction profile of BPA at 300 °C in the absence of catalyst (Fig. 9) revealed a consecutive reaction pathway in which the C_{arom}—Cα bond was cleaved to yield phenol and 4-isopropenylphenol. The latter compound was subsequently hydrogenated into 4-isopropylphenol.

Since no catalyst was added in the reactor, these results suggested that hydrogen could be produced by dehydrogenation of ethanol at 300 °C, either through a thermal reaction or catalysed by the Hastelloy reactor walls.

Fig. 10 exemplifies the effect of Pt/C catalyst on the reaction pathway: hydrogenation of 4-isopropenylphenol was now so rapid that this intermediate was not detected anymore, while phenol and 4-isopropylphenol were now formed quantitatively at similar rates. The rate constant for BPA disappearance, however, was barely modified by the catalyst presence (0.0088 min⁻¹ for uncatalyzed reaction, vs. 0.011 min-1 with Pt/C catalyst).

The apparent activation energy for the conversion of BPA was calculated using similar runs performed at 250 and 275 °C (data not shown) and amounted to 77 kJ/mol. Whatever the reaction temperature, phenol and 4-isopropylphenol were the only detected products.

In the bisphenol F (BPF) molecule, the Cα carbon is a secondary carbon, in contrast with the quaternary carbon of BPA bearing two methyl groups. The C_{arom}—Cα bond of BPF was nevertheless cleaved to yield roughly equimolar amounts of phenol and p-cresol (Fig. 11). BPF, however, was clearly less reactive than BPA under similar reaction conditions (compare Fig. 11 and Fig. 10), suggesting that the
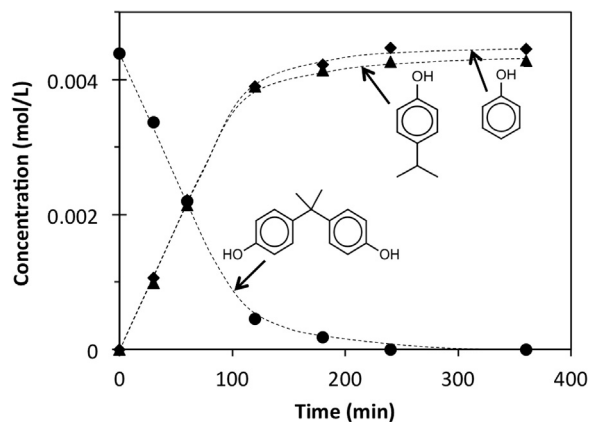

Fig. 10. Reaction profile of BPA in ethanol-water mixture. Conditions: 1 g/L BPA in 50 vol.% ethanol + 50 vol.% water, 18.77 mg Pt/C, 300 °C, 120 bar.
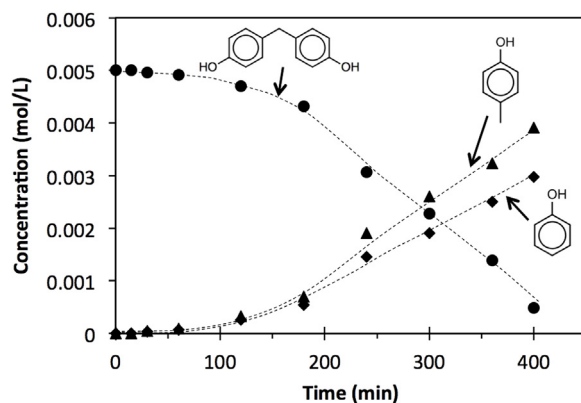

Fig. 11. Reaction profile of BPF in ethanol-water mixture. Conditions: 1 g/L BPF in 50 vol.% ethanol + 50 vol.% water, 18.77 mg Pt/C, 300 °C, 120 bar.
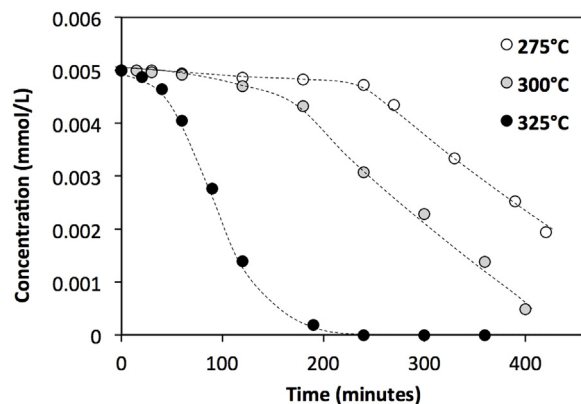

Fig. 12. Reaction profiles of BPF at three temperatures. Conditions: 1 g/L BPF in 50 vol.% ethanol + 50 vol.% water, 18.76 ± 0.04 mg Pt/C, 80 bar at 275 °C, 120 bar at 300 °C, 180 bar at 325 °C.

Cα substitution had an impact on the reactivity of the C_{arom}—Cα bond.

Similar tests carried out at 275 and 325 °C revealed that the disappearance profiles of BPF exhibited two different slopes, particularly noticeable at 275 °C and 300 °C (Fig. 12), which suggested an induction period before the reaction starts. This can be attributed to the fact that BPF is insoluble in water [25], in relation with the injection procedure of the reactants in the autoclave: BPF dissolved in ethanol is injected in the pre-heated autoclave containing the catalyst in suspension in water, using a high pressure pump. This
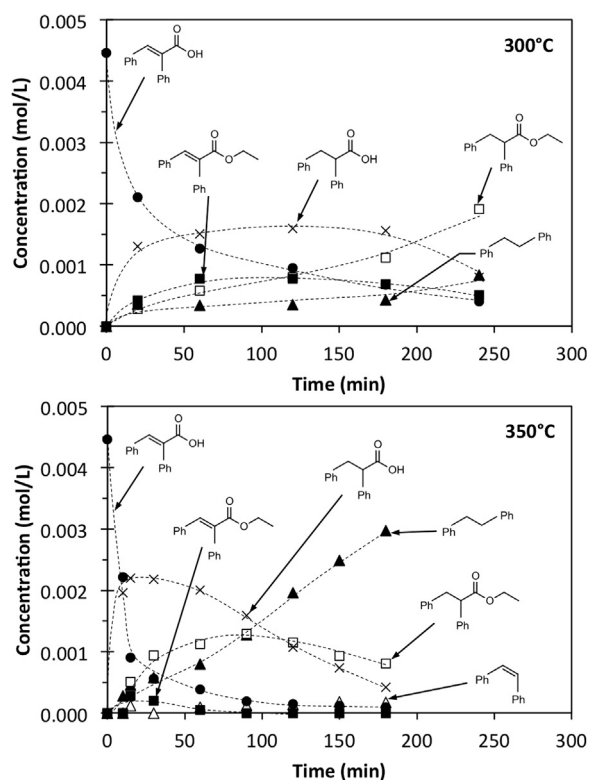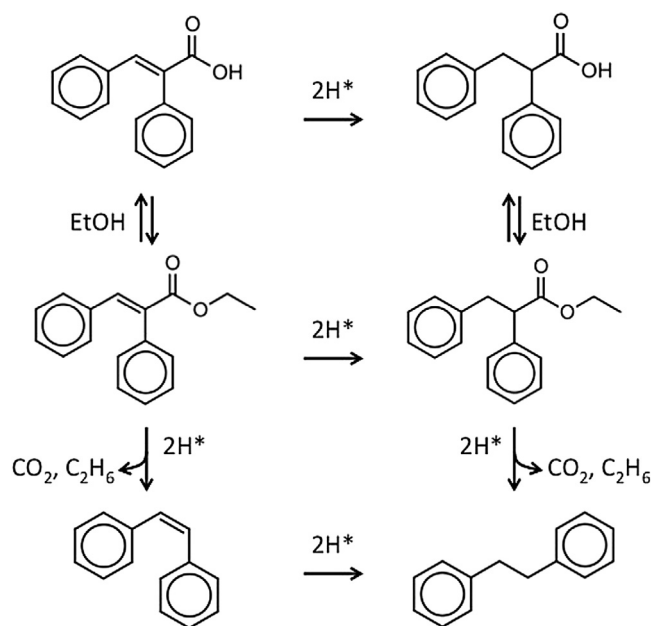
Fig. 13. Reaction profile of PCA in ethanol-water mixture. Conditions: 1 g/L PCA in 50 vol.% ethanol + 50 vol.% water, 18.78 mg Pt/C, 300 °C, 120 bar or 18.75 mg Pt/C, 350 °C, 240 bar.

Scheme 3. Reaction network for PCA in water-ethanol mixture.

probably led to an initial precipitation of BPF in the autoclave, when the ethanol solution blends with water, followed by re-dissolution in the ethanol/water mixture and diffusion of BPF to the catalyst active sites before it started to react. During this induction period, the samplings probably contained a colloidal suspension of BPF, which had nevertheless re-dissolved a few hours later when the samples were injected in the GC–MS for analysis.

Therefore, regardless of the induction period, the reactivity of BPF at 300 °C was not very different from that of BPA, which minimizes the impact of the Cα substituents. However, since the reaction onset could not be precisely defined in these experiments, the apparent activation energy for the reaction of BPF was not calculated.

The β1 linkage of lignin can be represented by the bibenzyle (BBZ) molecule. Tests performed on BBZ at temperatures up to 350 °C in the presence of Pt/C catalyst revealed that this compound was totally unreactive under the present conditions and remained unconverted (data not shown), highlighting indirectly that the presence of electron-donating oxygenated groups on the aromatic rings has probably an important role in increasing the reactivity of lignin model compounds.

Likewise BBZ, the β1 bond of α-phenylcinnamic acid (PCA) was not cleaved, but this compound reacted rapidly at 300 °C to yield its C=C hydrogenated product 2,3-diphenylpropanoic acid (Fig. 13). The two carboxylic acids were in equilibrium with their corresponding ethyl esters. We observed similarly in a previous study that linoleic acid was rapidly esterified in ethanol/water mixture [8], whereas Ma et al. also reported that many ethyl esters of carboxylic acids were formed during the depolymerisation of Kraft lignin in supercritical ethanol [18]. Small amounts of bibenzyle (BBZ) were also formed, which corresponded to the final reaction product, since it was shown previously that this compound did not react under these conditions.

At 350 °C, the reaction of PCA was faster and bibenzyle became the major product after 180 min of reaction. Small amounts of cis-1,2-diphenylethene (cis-stilbene) were also detected. The calculated apparent activation energy for the reaction of PCA was found equal to 62 kJ/mol, but it is related to C=C hydrogenation, not to the cleavage of the β1 linkage.

By analogy with our previous studies on linoleic acid, showing that the hydrogenolysis of the ester to form heptadecane was favoured over the direct decarboxylation of the acid, a similar reaction pathway for PCA is proposed in Scheme 3. The present results, obtained with another organic acid, confirmed the elimination of the carboxylic group as a possible deoxygenation pathway for lignin model compounds.

Among the two C—C model linkages studied here, only α1 bonds were cleaved under the present reaction conditions, while the β1 bonds were found unreactive. However, the two model compounds for α1 bonds (BPA and BPF) both carry OH substituents on the aromatic rings, whereas the two model compounds for β1 bonds (BBZ and PCA) do not. Therefore it would be interesting to investigate the reactivity of β1 model compounds with −OH or −OR groups on the aromatic rings.

Table 1 summarizes the results obtained with the lignin model compounds considered in this study.

4. Conclusion

The reactions of eight model compounds of lignin emulating various C—O and C—C lignin linkages have been investigated under catalytic hydrothermal conditions (275–350 °C, Pt/C catalyst) in ethanol/water mixtures, ethanol being used as H-donor. C—O model bonds of lignin were cleaved by H-transfer hydrogenolysis. The order of reactivity of C—O model bonds was found: β—O—4 > α—O—4 » 4—O—5, the 4—O—5 bond exhibiting a very low reactivity. This order was in agreement with the apparent activation energy calculated for the cleavage of the corresponding bonds: 55–58, 99 and 130 kJ/mol., respectively. Phenolic hydroxyl and methoxyl groups were totally unreactive, whereas aliphatic hydroxyl groups could be eliminated by dehydration, leading to an overall partial deoxygenation. β-1 model C—C bonds were not cleaved, although carboxyl groups on Cα could be eliminated by

Table 1
Summary of studied model compounds and their reactions (k' is the pseudo 1st order rate constant at 300 °C)

Compound	Model bond	cleavage/deoxygenation	Ea (kJ/mol)	k' (min⁻¹) at 300 °C	Effect of Pt/C catalyst	
					on reaction rate	on reaction selectivity
BPE	α—O—4	yes/no	99	0.014	yes	no
4PP	4—O—5	yes/no	130	0.0002	no	no
DHPMPE	β—O—4	yes/no	58	0.155	no	no
GGGE	β—O—4	yes/yes	55	0.215	no	yes
BPA	α—1	yes/no	77	0.011	yes	yes
BPF	α—1	yes/no	–	–	yes	no
BBZ	β—1	no/–	–	–	no	no
PCA	β—1	no/yes	–	–	yes	yes

decarboxylation. In contrast, α-1 model C—C bonds were also cleaved by H-transfer hydrogenolysis. The cleavage of C—O and C—C bonds obtained by H-transfer hydrogenolysis in water-ethanol mixtures was always very selective with only intermediate products detected if the reaction was stopped before full completion, but no formation of by-products or decomposition products.

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